An International Journal
computers & mathematics with applications

PERGAMON Computers and Mathematics with Applications 41 (2001) 1515–1520
www.elsevier.nl/locate/camwa

Electron Attraction and the Chemical Bond

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(Received and accepted August 2000)

Abstract—Using electron attraction, we produce three sets of initial conditions for the ground state H_2 molecule which yield, over one complete period, bond lengths and vibrational frequencies which are correct to within 1%. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords—Chemical bond, Hydrogen molecule, Electron attraction.

1. INTRODUCTION

As important as the chemical bond is, there is as yet no universally accepted theory of bonding. Historically, problems with valence bond theory resulted in its being replaced by molecular orbital theory, which in turn, was improved upon by resonance theory [1–3]. Resonance theory lost a number of adherents when it had to be refined by hybrid resonance [4,5]. The situation is summarized succinctly by Mahan [2] as follows: "... bonding phenomena are so complex that there exist 'violations' of almost every simple bonding rule".

In order to better understand the failure of Newtonian dynamics in the simulation of molecular bonding, we simulated the dynamical behavior of the simplest molecule, i.e., ground state H_2. For this molecule, the total energy is $E = -(50.7289)10^{-12}$ erg, the average bond length is $d = 0.742$ Å, and the average vibrational frequency is $f = (1.318)10^{14}$ H [6]. These are experimental results. We then assumed that the forces were Coulombic and that the electrons and the protons interact in accordance with Newtonian dynamics. Using numerical methodology which conserves the same energy, linear momentum, and angular momentum as any conservative Newtonian system [7], we simulated the electron and proton motions from a variety of fixed initial data. The best result we obtained was $d = 0.76$ Å, $f = (2.1)10^{14}$ H, in which the frequency is in error by 67% [8]. We then understood why the Newtonian formulation was unacceptable.

Instead of the going directly into a quantum mechanical formulation, we continued with the Newtonian formulation but introduced a common device from quantum mechanics, namely, *shielding*, in which the two electrons repel with an effective force which is less than that of full Coulombic repulsion. This repulsive force was decreased by the factor 0.9 and the resulting conservative calculations enabled us to decrease the frequency error to 62%, while the bond length remained in an acceptable range. Motivated by this decrease in error, we then decreased

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PII: S0898-1221(01)00116-X

the factor 0.9 incrementally through the values 0.5, 0.1, 0.01, 0.001, 0.0001. The error in frequency decreased constantly. For 0.0001, the frequency error dropped to 35% while the bond length remained in an acceptable range. We then took a purely mathematical leap across zero and multiplied the Coulombic force between the electrons, in order, by -0.0001, -0.001, -0.01, -0.1, -1.0. The frequency error constantly decreased while the bond length remained in an acceptable range. Indeed, for the case -1.0, both the frequency and bond length were in error by less than 5%. However, multiplication of the Coulombic force between the electrons by -1.0 means that the electrons are attracting, not repelling.

In discussing this seemingly strange result with colleagues in physics, it was pointed out that attraction between like charges, real or apparent, was not unknown in the literature [9–12] and that electron attraction was fundamental to the Bardeen, Cooper and Schrier [13] theory of superconductivity.

We next showed that electron attraction did yield correct bond lengths and vibrational frequencies for all the diatomic molecules through O_2 and even accounted for the 104.5° bond angle of the water molecule [14].

It might be pointed out also that though it is commonly thought that electrons always repel, there is no experimental evidence to support this behavior within any molecule [15].

Our purpose in this paper is to show that one can do much better than obtain molecular diameters and vibrational frequencies which lie only within the 5% error range. We concentrate only on the ground state H_2 molecule.

2. MATHEMATICAL, COMPUTATIONAL, AND PHYSICAL CONSIDERATIONS

For the ground state H_2 molecule, the energy is

$$E = -(50.7289)10^{-12}\,\text{erg}, \tag{2.1}$$

the average bond length d is

$$d = 0.742\,\text{Å}, \tag{2.2}$$

the average vibrational period t^* is

$$t^* = (0.759)10^{-14}\,\text{sec}, \tag{2.3}$$

and the average vibrational frequency is

$$f = \frac{1}{t^*} = (1.318)10^{14}\,\text{H}. \tag{2.4}$$

Now, let P_1, P_3 be the electrons and P_2, P_4 the protons. At any time t, let P_i, $i = 1, 2, 3, 4$, be located at $\boldsymbol{r}_i = (x_i, y_i, z_i)$, have velocity $\boldsymbol{v}_i = (\dot{x}_i, \dot{y}_i, \dot{z}_i)$, and have acceleration $\boldsymbol{a}_i = (\ddot{x}_i, \ddot{y}_i, \ddot{z}_i)$. Then the classical equations of motion under Coulombic forces are

$$m_i \boldsymbol{a}_i = \sum_{\substack{j=1 \\ j \neq i}}^{4} \frac{e_i e_j}{r_{ij}^2} \frac{\boldsymbol{r}_{ji}}{r_{ij}}, \qquad i = 1, 2, 3, 4, \tag{2.5}$$

in which $\boldsymbol{r}_{ji}$ is the vector from P_j to P_i, $r_{ij} = \|\boldsymbol{r}_{ij}\|$, and

$$e_1 = -e_2 = e_3 = -e_4 = (-4.8028)10^{-10}\,\text{esu}, \tag{2.6}$$

$$m_1 = m_3 = (9.1085)10^{-28}\,\text{g}, \tag{2.7}$$

$$m_2 = m_4 = (16724)10^{-28}\,\text{g}. \tag{2.8}$$

We now introduce electron attraction into (2.5) simply by changing the sign of e_1e_3 to $-e_1e_3$. For computational convenience, we set $\boldsymbol{R}_i = (X_i, Y_i, Z_i)$ and use the transformations

$$\boldsymbol{R}_i = 10^{12}\boldsymbol{r}_i, \tag{2.9}$$

$$T = 10^{22}t. \tag{2.10}$$

Note that

$$\boldsymbol{V}_i = \left(\frac{dX_i}{dT}, \frac{dY_i}{dT}, \frac{dZ_i}{dT}\right) = 10^{-10}\boldsymbol{v}_i, \tag{2.11}$$

and observe that the energy to be conserved is given by

$$\begin{aligned} E = {} & \frac{1}{2}(9.1085)10^{-28}\left(v_1^2 + v_3^2\right) + \frac{1}{2}(16724)10^{-28}\left(v_2^2 + v_4^2\right) \\ & + (23.06689)10^{-20}\left(-\frac{1}{r_{12}} - \frac{1}{r_{13}} - \frac{1}{r_{14}} - \frac{1}{r_{23}} + \frac{1}{r_{24}} - \frac{1}{r_{34}}\right), \end{aligned} \tag{2.12}$$

or, in the RT variables,

$$\begin{aligned} E = {} & \frac{1}{2}(9.1085)10^{-8}\left(V_1^2 + V_3^2\right) + \frac{1}{2}(16724)10^{-8}\left(V_2^2 + V_4^2\right) \\ & + (23.06689)10^{-8}\left(-\frac{1}{R_{12}} - \frac{1}{R_{13}} - \frac{1}{R_{14}} - \frac{1}{R_{23}} + \frac{1}{R_{24}} - \frac{1}{R_{34}}\right). \end{aligned} \tag{2.13}$$

Initially, we set P_1 at $(X_1, 0, Z_1)$, P_2 at $(X_2, 0, 0)$, P_3 at $(X_1, 0, -Z_1)$, and P_4 at $(-X_2, 0, 0)$. The velocities $\boldsymbol{V_2}$ and $\boldsymbol{V_4}$ are taken to be zero, while the velocities of P_1 and P_3 are taken to be $(0, VY, 0)$, $(0, -VY, 0)$, respectively. The value VY is chosen to be positive and is determined from (2.1) and (2.13).

3. GENERATION OF DESIRED INITIAL DATA

There are several ways in which one might approach the development of better results for vibrational frequency and bond length than were obtained previously. First, one could use a statistical approach, but here the reliability of our data sets would always be in question, so this was disregarded. Second, we could explore the possibility that -1.0 was not the correct factor in previous calculations, but this would violate the interesting conclusion that the electrons were attracting. We decided then that the approach to use was to generate at least one data set which, when used as initial data, yielded results in bond length and frequency which were both in error by less than 1%, and this was done as follows.

Extensive previous calculations [16] yielded results in which at least one of the bond distance d or the vibrational frequency f was in error between 3% and 4%, while the other was in error between 1% and 2%. In addition, those calculations indicated that the better results followed in the ranges

$$500 \le X_1 \le 1500, \qquad 2500 \le Z_1 \le 3500, \qquad \text{and} \qquad 3000 \le X_2 \le 4000.$$

We then ran 125 cases for all possible combinations of

$$\begin{aligned} X_1 &= 500,\ 750,\ 1000,\ 1250,\ 1500, \\ Z_1 &= 2500,\ 2750,\ 3000,\ 3250,\ 3500, \\ X_2 &= 3000,\ 3200,\ 3400,\ 3600,\ 4000, \end{aligned}$$

for 160,000,000 time steps with $\Delta T = 1.0$. Our best results were found for the two very similar cases

$$\begin{aligned} &\text{Case A: } X_1 = 1000,\ Z_1 = 2750,\ X_2 = 3600, \\ &\text{Case B: } X_1 = 1250,\ Z_1 = 2750,\ X_2 = 3600. \end{aligned}$$

Table 1. Case A results.

	d_1 (Å)	d_2 (Å)	$t\,(10^{-14}\text{s})$
1	0.7195		0.00639890
2		0.7581	0.33471786
3	0.7205		0.71817311
4		0.7587	1.04661974
5	0.7190		1.43060966
6		0.7598	1.78646103
7	0.7173		2.16995961
8		0.7614	2.56866011
9	0.7170		2.91077300
10		0.7606	3.29435090
11	0.7187		3.66422314
12		0.7607	4.02032296
13	0.7179		4.39104043
14		0.7588	4.73211116

Finally, we ran each of these cases for 500,000,000 time steps and the results of these calculations are now described as follows.

In general, the motion of P_2 and P_4 along the X axis is not periodic. Hence, in Table 1, we have recorded for Case A the minimum diameters d_1(Å) of $\|P_2P_4\|$, the maximum diameters d_2(Å) of $\|P_2P_4\|$, and the time $t(10^{-14}s)$ at which each occurs. In the table, the cycle described on lines 9–11 has the following properties. The average bond length is

$$d = \frac{1}{2}\left[\frac{1}{2}(0.7170 + 0.7187) + 0.7606\right] = 0.7392\,\text{Å}, \tag{3.1}$$

which is in error by 0.0028 Å. Hence, it is in error by 0.38%. In addition, the time for the oscillation is

$$t = (3.66422314 - 2.91077300)10^{-14} = (0.75345014)10^{-14}\,\text{s}, \tag{3.2}$$

which yields a frequency of

$$f = \frac{1}{t} = (1.327227838)10^{14}\,\text{H}. \tag{3.3}$$

Thus, the frequency is in error by $(0.009227838)10^{14}$ s, or is in error by 0.70%. Since this cycle satisfies the criteria we have set, we reran Case A again until $t = (2.91077300)10^{-14}$, i.e., until $T = 291077300$, which is the time at which line nine results, and recorded the positions and velocities at this time. These results are in Table 2 and constitute the initial data one can choose to have the results described in (3.1)–(3.3).

Table 2. Initial data.

	P_1	P_2	P_3	P_4
X	1160.43309324	3584.97355195	1160.43309324	−3585.14830737
Y	2114.25751690	0.0	−2114.25751690	0.0
Z	10187.52101476	0.0	−10187.52101476	0.0
VX	−0.00045049879	0.00000024539	−0.00045049879	0.00000024533
VY	0.01100637074	0.0	−0.01100637074	0.0
VZ	−0.00268616466	0.0	0.00268616466	0.0

Table 3. Case B results.

	d_1 (Å)	d_2 (Å)	$t\,(10^{-14}\text{s})$
1	0.7195		0.00617089
2		0.7785	0.35766735
3	0.7213		0.73688965
4		0.7795	1.10919061
5	0.7198		1.48061362
6		0.7781	1.86741202
7	0.7220		2.21217636
8		0.7770	2.61176019
9	0.7206		2.96914518
10		0.7765	3.32718780
11	0.7188		3.69901987
12		0.7756	4.07032030
13	0.7182		4.44155237
14		0.7760	4.79932162

Table 4. Initial data.

	P_1	P_2	P_3	P_4
X	−2.55126990	3898.42649704	−2.55126990	−3897.06212690
Y	−2860.42353647	0.0	2860.42353647	0.0
Z	783.41346296	0.0	−783.41346296	0.0
VX	0.00064036456	−0.00000034885	0.00064036456	−0.00000034868
VY	0.01409985112	0.0	−0.01409985112	0.0
VZ	0.03760562563	0.0	−0.03760562563	0.0

In Table 3, we have recorded for Case B the minimum diameters d_1(Å) of $\|P_2P_4\|$, the maximum diameters d_2(Å) of $\|P_2P_4\|$, and the time $t(10^{-14}\text{s})$ at which each occurs. In that table, the cycle described in lines 4–6 has the following properties. The average bond length is

$$d = \frac{1}{2}\left[\frac{1}{2}(0.7795 + 0.7781) + 0.7198\right] = 0.7493\,\text{Å}, \tag{3.4}$$

which is in error by 0.0073 Å. Hence, it is in error by 0.98%. In addition, the time for the oscillation is

$$t = (0.7582214)10^{-14}\,\text{s}, \tag{3.5}$$

which yields a frequency of

$$f = \frac{1}{t} = (1.319)10^{14}\,\text{H}. \tag{3.6}$$

Thus, the frequency is in error by 0.076%. Since this cycle satisfies the criteria we have set, we reran Case B again until $t = (1.10919061)10^{-14}$, i.e., until $T = 110919061$, which is the time at which line 4 results, and recorded the positions and velocities at this time. These results are in Table 4 and constitute the initial data one can choose to have the results described in (3.4)–(3.6).

However, note that in Table 3, the cycle described by lines 7–9 also yields the desired result. The average bond length is

$$d = \frac{1}{2}\left[\frac{1}{2}(0.7220 + 0.7206) + 0.7770\right] = 0.749\,\text{Å}, \tag{3.7}$$

which is in error by 0.007 Å. Hence, it is in error by 0.94%. In addition, the time for the oscillation is

$$t = (0.75696882)10^{-14}\,\mathrm{s}, \tag{3.8}$$

which yields a frequency of

$$f = \frac{1}{t} = (1.321)10^{14}\,\mathrm{H}. \tag{3.9}$$

Thus, the frequency is in error by 0.23%. Since this cycle satisfies the criteria we have set, we reran Case B again until $t = (2.21217636)10^{-14}$, i.e., until $T = 221217636$, which is the time at which line 7 results, and recorded the positions and velocities at this time. These results are in Table 5 and constitute the initial data one can choose to have the results described in (3.7)–(3.9). Thus, Table 5 provides still a third set of initial data which yields errors in bond length and frequency which are both less than 1%.

Table 5. Initial data.

	P_1	P_2	P_3	P_4
X	−2689.03286407	3611.99727399	−2689.03286407	−3607.70659228
Y	9997.62852987	0.0	−9997.62852987	0.0
Z	−1461.84949217	0.0	1461.84949217	0.0
VX	0.00024897353	−0.00000013558	0.00024897353	−0.00000013562
VY	−0.00375156069	0.0	0.00375156069	0.0
VZ	−0.01131566475	0.0	0.01131566475	0.0

4. REMARKS

First, some remarks are in order about the computations. All were performed on a Digital Alpha 275 personal scientific computer in double precision. At each time step, the calculated energy was $-(50.7289)10^{-12}$ erg. Accuracy was spot checked with $\Delta T = 0.2$. The Newtonian iteration tolerances were 10^{-10} for position and 10^{-12} for velocity. The run time for 160,000,000 time steps was three hours.

Also, it is felt that the classical simulation is valid since the real time of application is small [17].

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